CLAIMS

SUB A1 > 1. ~~A method of three-dimensional printing, comprising: providing a first layer of dry particulate material comprising an ionic reactant; dispensing a homogeneous fluid onto a first region of the first layer, the fluid comprising an ionic reactant; and allowing an ion exchange reaction to occur between the particulate reactant and the reactant in the fluid, the reaction causing a solidified material to form in the first region.~~

2. The method of claim 1, wherein the reactant in the fluid is an electrolyte.

3. The method of claim 2, wherein the electrolyte is a polyelectrolyte.

4. The method of claim 3, wherein the polyelectrolyte is a cationic polyelectrolyte.

5. The method of claim 4, wherein the cationic polyelectrolyte is selected from the group consisting of polyallylamine hydrochloride, polybutylaminoethyl methacrylate, polyethyleneimine, polyvinyl pyridine and poly diallyldimethylammonium chloride.

6. The method of claim 3, wherein the polyelectrolyte is an anionic polyelectrolyte.

7. The method of claim 6, wherein the anionic polyelectrolyte is selected from the group consisting of sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid and copolymer of sodium styrene sulfonate with maleic anhydride.

8. The method of claim 6, wherein the particulate ionic reactant is a cationic reactant.

9. The method of claim 8, wherein the cationic reactant is selected from the group consisting of Empresol N, Unicat KC1420, Unicat C3T, PENCAT 600, APOLLO 4280, polyallylamine hydrochloride, polybutylaminoethyl methacrylate, polyethyleneimine, polyvinyl pyridine, poly diallyldimethylammonium chloride, aminosilane-functionalized glass beads.

10. The method of claim 4, wherein the particulate ionic reactant is an anionic reactant.

11. The method of claim 10, wherein the anionic reactant is selected from the group consisting of Astro-gum 3010, Astro-gum 21, sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid and copolymer of sodium styrene sulfonate with maleic anhydride.

12. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material, at least a portion of the particulate material comprising particles having a reactive coating; and

dispensing a fluid onto a first region of the first layer.

13. The method of claim 12, further comprising the step of allowing a reaction to occur between the reactive coating and a reactant in the fluid, the reaction causing a solidified material to form in the first region.

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14. The method of claim 12, wherein the particles having a reactive coating each comprise an inert particle having a reactive coating.

15. The method of claim 14, wherein the reactive coating is adsorbed on the inert particle.

16. The method of claim 14, wherein the reactive coating is covalently bonded to the

inert particle.

17. The method of claim 12, wherein the reactive coating is selected from the group consisting of phenolic precursors, vinyl groups, acids, bases, isocyanates, cyanoacrylates, epoxides, amines, carboxylic acids, hydroxyl groups, acetates, amides and esters.

18. The method of claim 12, wherein the particulate material further comprises a reactant that is soluble in the fluid.

19. The method of claim 13, wherein the reaction is an ion exchange reaction.

20. The method of claim 13, wherein the reaction is a hydrogen-bonding reaction.

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21. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material comprising a reactant selected from the group consisting of metals, minerals and ceramic oxides;

dispensing a homogeneous fluid onto a first region of the first layer, the fluid comprising a reactant; and

allowing a reaction to occur between the particulate reactant and the reactant in the fluid, the reaction causing a solidified material to form in the first region.

22. The method of claim 21, wherein the reactant in the fluid is a polymer capable of solidification.

23. The method of claim 22, wherein the solidification occurs by ionic bonding.

24. The method of claim 22, wherein the solidification occurs by hydrogen bonding.

25. The method of claim 22, wherein the solidification occurs by cross-linking.

26. The method of claim 22, wherein the reactant is selected from the group consisting of sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic

acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid and copolymer of sodium styrene sulfonate with maleic anhydride.

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27. The method of claim 22, wherein the metal is selected from the group consisting of iron, copper, carbon steel, stainless steel, aluminum, brass, molybdenum, tungsten, magnesium, and cobalt.

28. The method of claim 26, wherein the ceramic oxide is selected from the group consisting of alumina (Al_2O_3), anatase (TiO_2), silicon dioxide, aluminum silicate and glass.

29. The method of claim 26, wherein the mineral is limestone (CaCO3), magnetite, calcium silicate ($CaSiO_4$), hydrous calcium sulfate ($CaSO_4 \cdot 2H_2O$), hydrated lime ($Ca(OH)_2$) and calcium phosphate.

30. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material comprising a particles having a reactive surface;

dispensing a fluid onto a first region of the first layer, the fluid comprising a reactant; and

allowing a reaction to occur between the reactive polymer and the reactant in the fluid, the reaction causing a solidified material to form in the first region.

31. The method of claim 30, wherein the reactant in the fluid is a monomer and the particulate material further comprises an initiator.

32. The method of claim 31, wherein the monomer is selected from the group consisting of a vinylic monomer, an acrylic monomer and a dienic monomer.

33. The method of claim 32, wherein the monomer is selected from the group consisting of acrylic acid, methacrylic acid, acrylamide and styrene.

34. The method of claim 31, wherein the reactive polymer is selected from the group consisting of an unsaturated polyester, polybutadiene, polyisoprene, an unsaturated polyurethane and copolymers thereof.

35. The method of claim 31, wherein the initiator is selected from the group consisting of potassium persulfate, ammonium persulfate, sulfuric acid, perchloric acid, fluorosulfonic acid, trifluoromethylsulfonic acid, trifluroacetic acid, tin tetrachloride, aluminum trichloride, and boron trifluoride, potassium peroxodisulfate, ammonium persulfate with N,N,N',N'-tetramethylethylenediamine (TMEDA), 3-dimethylaminopropionitrile (DMAPN, potassium persulfate with 4,4-azobis(4-cyanovaleric acid), dibenzoyl peroxide, t-butyl perbenzoate and azobisisobutyronitrile.

36. The method of claim 30, wherein the particulate material comprising a reactive polymer includes inert particles having a reactive coating.

37. The method of claim 30, wherein the reactive coating is a polyol group.

38. The method of claim 37, wherein the reactant in the fluid is an isocyanate.

39. The method of claim 38, wherein the isocyanate is Bayhydur XP-7063.

40. The method of claim 36, wherein the reactive coating comprises sodium polystyrene sulfonate, sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid and copolymer of sodium styrene sulfonate with maleic anhydride.

41. The method of claim 40, wherein the reactant in the fluid is a cationic polyelectrolyte.

42. The method of claim 41, wherein the cationic polyelectrolyte is selected from the group consisting of polyallylamine hydrochloride, polybutylaminoethyl methacrylate, polyethyleneimine, polyvinyl pyridine and poly diallyldimethylammonium chloride.

43. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material comprising a reactant; and

dispensing a fluid onto a first region of the first layer, the fluid comprising a reactant capable of hydrogen-bonding with the particulate reactant.

44. The method of claim 43, further comprising the step of allowing hydrogen bonding to occur between the particulate reactant and the reactant in the fluid, the hydrogen bonding causing a solidified material to form in the first region.

45. The method of claim 44, wherein the particulate reactant is soluble in the fluid.

46. The method of claim 45, wherein the particulate reactant is a hydrogen-bond donor.

47. The method of claim 46, wherein the hydrogen-bond donor is selected from the group consisting of polymethacrylic acid, polyacrylic acid and polyvinyl alcohol.

48. The method of claim 46, wherein the reactant in the fluid is a hydrogen-bond acceptor.

49. The method of claim 48, wherein the hydrogen-bond acceptor is selected from the group consisting of polyethylene oxide, polyvinyl pyridine, polyethylene glycol and polyvinylpyrrolidone.

50. The method of claim 45, wherein the particulate reactant is a hydrogen-bond acceptor.

51. The method of claim 50, wherein the hydrogen-bond acceptor is selected from the group consisting of polyethylene oxide, polyvinyl pyridine, polyethylene glycol and

polyvinylpyrrolidone.

52. The method of claim 50, wherein the reactant in the fluid is a hydrogen-bond donor.

53. The method of claim 52, wherein the hydrogen-bond donor is selected from the group consisting of polymethacrylic acid, polyacrylic acid and polyvinyl alcohol.

54. The method of claim 43, wherein an adhesive/hydrogen-bonding agent combination is selected from the group consisting of polyvinyl alcohol/Borax, polyvinyl alcohol/polyethylene oxide and polyethylene oxide/polymethacrylic acid.

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55. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material comprising a reactant;

dispensing a fluid onto a first region of the first layer, the fluid comprising a reactant; and

allowing a reaction to occur between the particulate reactant and the reactant to form an adhesive, the reaction causing a solidified material to form in the first region.

56. The method of claim 55, wherein particulate reactant is a copolymer of octacrylamide/acrylates/butylaminoethylmethacrylate.

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57. The method of claim 56, wherein the reactant in the fluid is selected from the group consisting of 2-amino-2-methyl 1-propanol (AMP), 2-amino-2-methyl 1-3 propanediol (AMPD), 2-amino-2-ethyl 1-3-propanediol (AEPD), and a hydroxide.

58. The method of claim 57, wherein the hydroxide is selected from the group consisting of sodium hydroxide, potassium hydroxide, and ammonium hydroxide.

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59. The method of claim 55, wherein the particulate reactant is selected from the group consisting of urea, a phenolic resin and melamine.

60. The method of claim 59, wherein the reactant in the fluid is formaldehyde.

61. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material; and

dispensing a first fluid comprising an adhesive and a second fluid comprising a cross-linking agent onto a first region of the first layer; and

allowing a cross-linking reaction to occur, the reaction causing a solidified material to form in the first region.

62. The method of claim 61, wherein the adhesive is polyvinyl alcohol and the cross-linking agent is Borax.

63. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material; and

dispensing a first fluid comprising a hydrogen-bond donor and a second fluid comprising a hydrogen-bond acceptor onto a first region of the first layer.

64. The method of claim 63, further comprising the step of allowing hydrogen bonding to occur between the hydrogen-bond donor and acceptor, the hydrogen bonding causing a solidified material to form in the first region.

65. The method of claim 64, wherein the hydrogen-bond donor is selected from the group consisting of polymethacrylic acid, polyacrylic acid and polyvinyl alcohol.

66. The method of claim 64, wherein the hydrogen-bond acceptor is selected from the group consisting of polyethylene oxide, polyvinyl pyridine, polyethylene glycol and polyvinylpyrrolidone.

67. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material;

dispensing a first fluid comprising a first reactant and a second fluid comprising a second reactant onto a first region of the first layer; and

allowing a reaction to occur between the first and second reactants to form an

adhesive.

68. The method of claim 67, wherein the formation of the adhesive causes a solidified material to form in the first region.

69. The method of claim 68, wherein the first reactant is an isocyanate.

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70. The method of claim 69, wherein the isocyanate is Bayhydur XP-7063.

71. The method of claim 69, wherein the second reactant is a polyol.

72. The method of claim 71, wherein the polyol is selected from the group consisting of glycerol, sorbitol, erythritol and epoxy-functionalized glass beads.

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73. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material comprising an adhesive;

dispensing a first fluid onto the first layer to dissolve the adhesive;

dispensing a fluid solidifying agent onto a first region of the first layer; and

allowing a reaction to occur between the first fluid and the solidifying agent, the reaction causing a solidified material to form in the first region.

74. The method of claim 73, wherein the particulate adhesive is octacrylamide/acrylates/butylaminoethylmethacrylate copolymer.

75. The method of claim 74, wherein the first fluid is selected from the group consisting of 2-amino-2-methyl 1-propanol (AMP), 2-amino-2-methyl 1-3 propanediol (AMPD), 2-amino-2-ethyl 1-3-propanediol (AEPD), sodium hydroxide, potassium hydroxide, and ammonium hydroxide.

76. The method of claim 75, wherein the solidifying agent is an acid.

77. The method of claim 76, wherein the acid is selected from the group consisting of hydrochloric acid, citric acid, succinic acid, adipic acid, polyacrylic acid,

polymethacrylic acid, and polyvinyl sulfonic acid.

78. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material;

dispensing a fluid monomer onto the first layer;

dispensing a fluid comprising an initiator onto a first region of the first layer; and

allowing polymerization to occur, the polymerization causing a solidified material to form in the first region.

79. The method of claim 78, wherein the initiator is cationic.

80. The method of claim 79, wherein the cationic initiator is selected from the group consisting of sulfuric acid, perchloric acid, fluorosulfonic acid, trifluoromethylsulfonic acid, trifluroacetic acid, tin tetrachloride, aluminum trichloride, and boron trifluoride.

81. The method of claim 79, wherein the monomer is selected from the group consisting of isobutene, alkenes, alkyl-vinyl ethers, vinylacetals, dienes, styrene, N-vinyl carbazole, beta-pinene, oxiranes, N-substituted aziridines, lactams and oxazolines.

82. The method of claim 78, wherein the initiator is a free-radical initiator.

83. The method of claim 82, wherein the free-radical initiator is selected from the group consisting of potassium peroxodisulfate, ammonium persulfate with N,N,N',N'-tetramethylethylenediamine (TMEDA) or 3-dimethylaminopropionitrile (DMAPN, potassium persulfate with 4,4-azobis(4-cyanovaleric acid), dibenzoyl peroxide, t-butyl perbenzoate and azobisisobutyronitrile.

84. The method of claim 82, wherein the monomer is selected from the group consisting of vinylic monomers, acrylic monomers, dienic monomers, acrylic acid, methacrylic acid and acrylamide.

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85. A method of three-dimensional printing, comprising:

providing a first layer of a dry particulate material comprising a first reactant and

a second reactant;

dispensing a fluid onto a region of the first layer; and

allowing a reaction between the first and second reactants to occur, the reaction causing a solidified material to form in the first region.

86. The method of claim 85, wherein at least one of the first and second reactants is soluble in the fluid.

87. The method of claim 86, wherein the first and second reactants are ionic reactants.

88. The method of claim 87, wherein the first reactant is an electrolyte.

89. The method of claim 88, wherein the first reactant is a polyelectrolyte.

90. The method of claim 89, wherein the first reactant is a cationic polyelectrolyte.

91. The method of claim 90, wherein the cationic polyelectrolyte is selected from the group consisting of polyallylamine hydrochloride, polybutylaminoethyl methacrylate, polyethyleneimine, polyvinyl pyridine and poly diallyldimethylammonium chloride.

92. The method of claim 89, wherein the first reactant is an anionic polyelectrolyte.

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93. The method of claim 92, wherein the anionic polyelectrolyte is selected from the group consisting of sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid, copolymer of sodium styrene sulfonate with maleic anhydride, polyethylene oxide, polyvinyl pyridine, polyethylene glycol and polyvinylpyrrolidone.

94. The method of claim 92, wherein the second reactant is a cationic reactant.

95. The method of claim 94, wherein the cationic reactant is selected from the group consisting of Empresol N, Unicat KC1420, Unicat C3T, PENCAT 600, APOLLO 4280, polyallylamine hydrochloride, polybutylaminoethyl methacrylate, polyethyleneimine, polyvinyl pyridine, poly diallyldimethylammonium chloride, aminosilane-functionalized glass beads.

96. The method of claim 90, wherein the second reactant is an anionic reactant.

97. The method of claim 96, wherein the anionic reactant is selected from the group consisting of Astro-gum 3010, Astro-gum 21, sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid and copolymer of sodium styrene sulfonate with maleic anhydride.

98. The method of claim 87, wherein the reaction is an ion exchange reaction.

99. The method of claim 85, wherein the first reactant is selected from the group consisting of metals, salts and ceramic oxides.

100. The method of claim 99, wherein the fluid is an acid.

101. The method of claim 100, wherein the acid is selected from the group consisting of acetic acid and hydrochloric acid.

102. The method of claim 100, wherein the second reactant is selected from the group consisting of a polymeric acid, sulfonated polystyrene, polyacrylic acid, polymethacrylic acid, polyvinyl sulfonic acid, alkali metal salts of polyacrylic acid, alkali metal salts of polymethacrylic acid, alkali metal salts of polyvinyl sulfonic acid, ammonium salt of polyvinyl sulfonic acid, ammonium salt of sulfonated polystyrene, ammonium salt of polyacrylic acid, ammonium salt of polymethacrylic acid and copolymer of sodium

styrene sulfonate with maleic anhydride.

103. The method of claim 102, wherein the metal is selected from the group consisting of iron, copper, carbon steel, stainless steel, aluminum, brass, molybdenum, tungsten, magnesium, and cobalt.

104. The method of claim 99, wherein the ceramic oxide is selected from the group consisting of alumina (Al_2O_3), anatase (TiO_2), silicon dioxide, aluminum silicate and glass.

105. The method of claim 99, wherein the mineral is selected from the group consisting of limestone (CaCO3), magnetite, calcium silicate ($CaSiO_4$), hydrous calcium sulfate ($CaSO_4 \cdot 2H_2O$), hydrated lime ($Ca(OH)_2$) and calcium phosphate.

106. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67; 73, 78 and 85, wherein the reaction occurs in the absence of an applied stimulus.

107. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85, wherein after the step of allowing the reaction to occur, the method further comprises the step of allowing the particulate material in the first region to solidify.

108. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85, wherein the first region of solidify material is contiguous with a second region of free-flowing particulate material.

109. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85,, further comprising the step of providing a second layer of the particulate material over the first layer after the dispensing step.

110. The method of claim 109, further comprising the step of dispensing the fluid onto a first region of the second layer.

111. The method of claim 109, further comprising the steps of providing subsequent

layers of the particulate material over a preceding layer, each providing step followed by the dispensing step.

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112. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85, wherein the particulate material comprises a mixture of inert particles and the particulate reactant.

113. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85, wherein the particulate material consists essentially of the particulate reactant.

114. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85, wherein the inert particle is selected from the group consisting of granular, powdered or fibrous materials.

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115. The method of any one of claims 1, 12, 21, 30, 43, 55, 61, 63, 67, 73, 78 and 85, wherein the inert particle is selected from the group consisting of a polymer, a ceramic, a metal, an organic material, an inorganic material, a mineral, clay and a salt.

116. The method of claim 115, wherein the polymer is selected from the group consisting of poly(methyl methacrylate), polystyrene, polyamide, polyester, a latex, polyethylene, polypropylene, polyurethane, polyvinyl chloride, polyvinyl acetate, cross-linked polyvinyl pyrrolidone, hydrophilic polyurethane, poly(ethylene terephthalate), thermoplastic urethane, styrene-acrylonitrile copolymer, thermoplastic polyolefin, an epoxy-based polymer, polyether, polyamine, a polyacid, a polycarbonate, a vinyl polymer, an aromatic polyamide, a diene polymer, poly(phenylene oxide), polysiloxane, polynorbornene, polyisoprene, a polyphenylene ether, styrene-butadiene block copolymer, acrylonitrile-butadiene-styrene, high impact polystyrene and copolymers thereof.

117. The method of claim 115, wherein the ceramic is selected from the group consisting of gypsum, limestone, clay, aluminum oxide, aluminum silicate, calcium silicate, silicon dioxide, titanium dioxide, glass, iron oxide, zinc oxide, magnetite, aluminum hydroxide, magnesium oxide, calcium phosphate, zirconium silicate, silicon

carbide, boron nitride, boron carbide and borosilicate.

118. The method of claim 115, wherein the organic material is selected from the group consisting of starch, cellulose, wood powder, wax, resin, bone, protein, carbohydrates, sugars, textile fibers and dietary fibers.

119. The method of claim 115, wherein the salt is selected from the group of sodium silicate, sodium carbonate, sodium bicarbonate, sodium borate, sodium chloride, sodium sulfate, potassium sulfate, potassium chloride, magnesium sulfate, magnesium chloride, potassium aluminum sulfate, sodium polyphosphate and sodium acetate, hydrous calcium sulfate, calcium phosphate, sodium silicate, and hydrated lime ($Ca(OH)_2$).

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